ESTCP

TECHNOLOGY USER'S MANUAL

Validation of Passive Sampling Devices for Monitoring of Munitions Constituents in Underwater Environments

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14. ABSTRACT
Traditional water sampling approaches have relied on collection of discrete "grab" samples that represent a single point in time. Despite improvements in technique, such as development of solid-phase extraction, collection of large volumes of water is required to satisfy the detection limit requirements of commonly used analytical methods. In cases where bulk (or filtered) water samples are shipped to the laboratory, the preservation and transport of large volumes of water can be problematic. On the other hand, the use of on-site automated sampling systems can be costly and difficult to maintain. These problems are amplified when the environmental concentrations vary significantly over time.

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Passive Sampling Devices, Munitions Constituents, Underwater Environments, GPS, Explosive Ordnance Disposal, Environmental Quantitation Limit, Laboratory Quantitation Limit, Munitions Response, Unexploded Ordnance, Underwater Military Munitions, Solid-phase Extraction

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Table of Contents

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1. Acronyms

1,3-DNB	1,3-dinitrobenzene
1,3,5-TNB	1,3,5-trinitrobenzene
2-ADNT	2-amino-4,6-dinitrotoluene
2,4-DANT	2,4-diamino-6-nitrotoluene
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
3,5-DNAL	3,5-dinitroaniline
4-ADNT	4-amino-2,6-dinitrotoluene
cm	Centimeter
DoD	Department of Defense
EOD	Explosive Ordnance Disposal
EPA	United States Environmental Protection Agency
EQL	Environmental Quantitation Limit
EST	Environmental Sampling Technologies, Inc.
ESTCP	Environmental Security Technology Certification Program
g	Gram
GPS	Global Positioning System
HLB	Hydrophilic-lipophilic balance (sorbent)
IPS	Integrative Passive Sampler
K_{ow}	Octanol-water partition coefficient
L	Liter
LQL	Laboratory Quantitation Limit
MC	Munitions Constituents
mL	Milliliter
MR	Munitions Response
NESDI	Navy's Environmental Security Development to Integration Program
ng	Nanogram
NOSSA	Naval Ordnance Safety and Security Activity
PES	polyethersulfone
POCIS	Polar Organic Chemical Integrative Sampler
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine (also Royal Demolition Explosive)
R_s	Sampling Rate
s	Second
SERDP	Strategic Environmental Research and Development Program
SPE	Solid-phase Extraction
SS	Stainless Steel
TNT	2,4,6-trinitrotoluene
TNX	hexahydro-1,3,5-trinitroso-1,3,5-triazine
TWA	Time-weighted Average
UXO	Unexploded Ordnance
UWMM	Underwater Military Munitions

2. POCIS development and description

Traditional water sampling approaches have relied on collection of discrete "grab" samples that represent a single point in time. Despite improvements in technique, such as development of solid-phase extraction (SPE; Buszewski and Szultka, M. 2012), collection of large volumes of water is required to satisfy the detection limit requirements of commonly used analytical methods. In cases where bulk (or filtered) water samples are shipped to the laboratory, the preservation and transport of large volumes of water can be problematic. On the other hand, the use of on-site automated sampling systems can be costly and difficult to maintain (Alvarez et al. 2007). These problems are amplified when the environmental concentrations vary significantly over time and thus numerous timed events are required to be collected to accurately assess concentration.

Environmental contamination of munition constituents (MC) can occur as episodic events including spills, storm water runoff, and varying hydrodynamic and environmental conditions associated with leakage of MC from breached unexploded ordnance (UXO; Wang et al. 2013) or direct exposure associated with low order detonations. When discrete water samples are only infrequently collected at a site where episodic contamination events are expected, a high probability that contaminants will not be detected exists, especially if the timing of the event is uncertain (Morrison et al. 2016). This problem is particularly relevant to hydrophilic organic compounds, such as 2,4,6-trinitrotoluene (TNT), TNT degradation products, and royal demolition explosive (RDX), as their residence times in aquatic systems are generally lower than hydrophobic organic compounds. However, transient but frequent occurrence of certain hydrophilic organic compounds in some scenarios may result in temporal changes in receiving water quality. Thus, there is a critical need for sampling and analytical methods capable of enhancing the detection and identification of MC in an integrated manner, which in turn, provides highly relevant time-weighted average (TWA) concentrations. Without this type of methodological advancement, investigators may face a daunting task in adequately assessing the environmental risks posed by this diverse class of chemicals. Achieving a TWA concentration from a single sample can dramatically reduce analytical costs compared to making numerous analytical measurements over a time-course.

Integrative passive samplers (IPS) are samplers for which no significant losses of accumulated residues occur during the exposure period. IPS concentrate ultra-trace to trace levels of chemicals over prolonged sampling periods, generally resulting in greater masses of sequestered chemicals than those recovered using grab sampling techniques. For example, using IPS for TNT and allowing 14 days of uptake would result in up to 21x more sensitivity. Consequently, the use of IPS is expected to result in increased analytical sensitivity and lower detection limits relative to those reported for most traditional methods. In addition, the use of IPS enhances the probability of the detection of chemicals that rapidly dissipate or degrade. Although a few passive sampling devices have been tested for hydrophilic organic compounds, the first and arguably best studied sampler reported for this chemical class is the polar organic chemical integrative sampler (POCIS), developed by David Alvarez and collaborators at the US Geological Survey, Columbia Environmental Research Center, Columbia, MO (Alvarez 1999; Alvarez et al. 2000).

The POCIS consists of a disk-like configuration of a solid-phase sorbent or a mixture of sorbents sandwiched between two microporous polyethersulfone (PES) membranes. High grade stainless steel (SS) rings are used to form a compression seal to prevent sorbent loss, as the PES membrane is not amenable to heat sealing (Alvarez et al. 2004). **Figure 1** depicts an array of POCIS supported on a threaded rod with an exploded view of the "membrane-sorbent-membrane sandwich", which comprises the functional component of the sampler. POCIS are commercially available from Environmental Sampling Technologies, Inc. (EST; St. Joseph, Missouri). The compression rings are made of a metallic material and thumb bolts and nuts are used to secure the rings to the membranes. The microporous PES membrane acts as a semipermeable barrier between the sorbent and the surrounding environment. It allows dissolved hydrophilic organic compounds to pass through to the sorbent, while particulates, microorganisms, and macromolecules with cross-sectional diameters greater than 100 nanometers are selectively excluded. Upon deployment of POCIS, water rapidly permeates the pore structure of PES membrane and makes direct contact with the sorbents. The average thickness of the hydrated PES membrane is approximately 130 micrometers. For a typical POCIS disk used in field studies, the effective surface area of the membranes in contact with exposure waters is 41 centimeters squared (cm^2) and the sorbent mass is ~ 228 milligrams (Alvarez et al. 2010).

Figure 1. POCIS (top) and commercially available field holder and canister for POCIS (bottom), available from EST (EST-Lab.com). Photos from Rosen et al. (2016).

Since their initial development, the use of POCIS as tools for field application have quickly become widespread, including use in large-scale monitoring studies, such as monitoring surface waters of lakes (Li et al. 2010, Sultana et al. 2017) and in rivers in the USA (McCarthy et al. 2007, 2012; Jones-Lepp et al. 2012). Although the majority of the sites investigated using POCIS are rivers, lakes and reservoirs, deployment in marine environments has been increasing (Bargar et al. 2012; Bueno et al. 2009; Harman et al. 2009, 2010, 2011, 2014). Recently, POCIS were also shown to be of high utility for exposure to MC in a marine environment (Rosen et al., 2016; Rosen et al. 2017).

POCIS are designed to sample the more water soluble organic chemicals with log octanol-water partition coefficients (K_{ow}) < 3 (Alvarez et al. 2010). This includes most pharmaceuticals, illicit drugs, polar pesticides, phosphate flame retardants, surfactants, metabolites and degradation products, as well as munitions constituents (MC) such as TNT, RDX and their major transformation products (Belden et al. 2015). **Table 1** lists the MC examined with POCIS to date, and some of their physicochemical characteristics.

Table 1. Physicochemical characteristics of munition constituents that have been studied using integrated passive sampling.

Analyte	Common Referred Name	CAS	Water Solubility, g/L*	Log K_{OW}*
2,4,6 -trinitrotoluene	TNT	118-96-7	0.13	1.6
2-amino-4,6-dinitrotoluene	2-ADNT	35572-78-2	0.42	1.94
4-amino-2,6-dinitrotoluene	4-ADNT	19406-51-0	0.42	1.91
2,4-diamino-6-nitrotoluene	2,4-DANT	6629-29-4	Not found	0.7
hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4	0.56	0.90
1,3,5-trinitroso-1,3,5-triazinane	TNX	13980-04-6	73	0.515
2,4-dinitrotoluene	2,4-DNT	121-14-2	0.27	1.98
2,6-dinitrotoluene	2,6-DNT	606-20-2	0.21	2.02
1,3,5-trinitrobenzene	1,3,5-TNB	99-35-4	0.092	1.16
1,3-dinitrobenzene	1,3-DNB	99-65-0	0.42	1.58

*Values for TNT, 2-ADNT, 4-ADNT, 2,4-DNT, 2,6-DNT, and RDX obtained from the United States Environmental Protection Agency (EPA; 2012). Values for TNX, 1,3,5-TNB and 1,3-DNB obtained from Scifinder (http://scifinder.cas.org; accessed 02/03/2017) and calculated using Advanced Chemistry Development Software V11.02 (ACD/Labs). Values for 2,4-DANT from Elovitz and Weber (1999). Conditions were modeled at 25 °C and pH 7.

Munitions have been tested and verified using the standard commercially available POCIS (http://est-lab.com/), which contains the sorbent Oasis® hydrophilic-lipophilic balance (HLB). Oasis® HLB is typically considered a universal sorbent in environmental analyses and has been used to extract a wide assortment of chemical classes from water. The chemical phase of the sorbent (polymeric poly [divinylbenzene-vinylpyrrolidone]) is available from several vendors in the SPE format, and is frequently used for active extraction of MCs from discrete water samples (DeTata et al 2013; Belden et al. 2015).

3. Theory and modeling

Accumulation of chemicals by IPS generally follows first order kinetics, which is characterized by an initial integrative phase, followed by curvilinear and equilibrium partitioning phases. For all phases of uptake, sampling rates (R_s; units of liters [L]/day) and sorbent-water partition coefficients (K_{sw}; units of milliliters [mL]/mL or grams [g]) are independent of exposure concentrations. During the integrative phase of uptake, a passive sampling device acts as an infinite sink for contaminants, and assuming constant exposure concentrations, residues are accumulated linearly relative to time. POCIS remains in the integrative phase of sampling during exposure periods of at least 30 days for compounds with a log K_{ow} greater than 1 (Alvarez et al. 2010) including many munitions (Belden et al 2015). An advantage of integrative samplers over equilibrium partition samplers is that TWA concentration of contaminants can be determined from sampler concentration data (assuming appropriate calibration data are available). Unlike samplers that rapidly achieve equilibrium (such as those commonly used for hydrophobic

compounds such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls), chemical residues from episodic release events are retained by integrative samplers at the end of the exposure period. Thus, integrative samplers have very small analyte loss rates and times to reach equilibrium are very large for most compounds evaluated (Alvarez et al. 2010).

Estimates of ambient environmental concentrations of analytes from the concentrations in a passive sampler can be made for most munitions as previous research has demonstrated that accumulation in the POCIS is proportional to environmental concentrations across environmentally relevant concentrations. In order to calculate environmental concentrations, the rate at which the analyte partitions from water to the POCIS must be experimentally determined for a given set of environmental conditions. These rates are relatively stable across temperature and salinity; however, adjustment may need to be made based on changes in flow across the sampler. The following equation for integrative (i.e., linear) sampling by an IPS:

$$C_w = \frac{N}{R_s t} \qquad \text{Equation 1}$$

In this equation, N is the amount of the chemical accumulated by the sampler (nanogram [ng]), R_s is the sampling rate (L day^{-1}), and t is the exposure time (day).

The POCIS is well-suited as a screening tool for determining the presence or absence of, sources, and relative amounts of chemicals at study sites, but the reasonable estimation of ambient water TWA concentrations requires knowledge of the sampling rate for each chemical measured. Recent studies have involved calculation of rates for many MC (**Table 2**).

4. Advantages and limitations compared to other sampling techniques

POCIS provides a means for determining the TWA concentrations of targeted chemicals that can be used in risk assessments to determine the biological impact of hydrophilic organic compounds on the health of the impacted ecosystem. Generating a sufficient number of samples to estimate TWA concentration by traditional methods may be logistically and financially imprudent as part of a regular monitoring program. Field studies have shown that POCIS has advantages over traditional sampling methods in sequestering and concentrating ultra-trace to trace levels of chemicals over time resulting in increased method sensitivity, ability to detect chemicals with a relatively short residence time or variable concentrations in the water (i.e., chemical/biological degradation, sorption, dissipation), and simplicity in use. POCIS has been successfully used worldwide under various field conditions ranging from stagnant ponds to shallow creeks to major river systems in both fresh and brackish water. Due to the quality of the data obtained, ease of use, and broad applicability to both chemical and biological assessments, the POCIS technique has the potential to become the standard for global water quality monitoring for munitions.

POCIS are designed to be relatively long-term (i.e., 2-4 week) integrative samplers. Generally, these samplers will provide little benefit over traditional discrete (grab) samples for study periods less than 5-7 days. Integration occurs over an extended time frame and shorter time

periods may suffer quantitatively from a lag effect. Time periods long than 21-28 days may also

Table 2. Compilation of all known studies conducted for MC sampling rates.

Analyte Name (common abbreviation)	CAS number	Sampling Rate Studies, mL/day	Study
2,4,6-trinitrotoluene (TNT)	118-96-7	93±13, ~0.1 cm/second (s); 25°C, salinity of 30 g/L	1
		Uncaged rate=81(flow rate)+14; caged rate=18(flow rate)-50	2
		125±18, ~0.1 cm/s; 25°C, salinity of 30 g/L	3
		97±16, static, 440±96 high flow; 23°C, salinity of 30 g/L	4
4-amino-2,6-dinitrotoluene (4-ADNT)	19406-51-0	104±19, ~0.1 cm/s, 25°C, salinity of 30 g/L	1
		81±17, static, 324±69 high flow; 23°C, salinity of 30 g/L	4
2-amino-4,6-dinitrotoluene (2-ADNT)	35572-78-2	97±21, ~0.1 cm/s, 25°C, salinity of 30 g/L	1
		111±24, static, 474±114 high flow; 23°C, salinity of 30 g/L	4
2,4-diamino-6-nitrotoluene (2,4-DANT)	6629-29-4	34±4, ~0.1 cm/s, 25°C, salinity of 30 g/L*	1
hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4	R_s (up to 14 days) - 129±29, equilibrium (longer than 28 days) 16400 mL/g (HLB/water), ~0.1 cm/s, 25°C, salinity of 30 g/L;	1
		Uncaged rate=5(flow rate)+0314; caged rate=8(flow rate)+270	2
		493±116, ~0.1 cm/s; 25°C, salinity of 30 g/L	3
		229±44, static, 515±170 high flow; 23°C, salinity of 30 g/L	4
2,4-dinitrotoluene (2,4-DNT)	121-14-2	Uncaged rate=3(flow rate)+52; caged rate=4(flow rate)+80	2
		82±6, ~0.1 cm/s; 25°C, salinity of 30 g/L	3
		50±9, static, 272±32 high flow; 23°C, salinity of 30 g/L	4
2,6-dinitrotoluene (2,6-DNT)	606-20-2	Uncaged rate=3(flow rate)+65; caged rate=4(flow rate)+7	2
		85±13, static, 359±63 high flow; 23°C, salinity of 30 g/L	4
3,5-dinitroaniline (3,5-DNAL)	618-87-1	50±14, static, 339±106 high flow; 23°C, salinity of 30 g/L	4
1,3,5-trinitrobenzene (1,3,5-TNB)	99-35-4	77±8, static, 329±56 high flow; 23°C, salinity of 30 g/L	4
1,3-dinitrobenzene (1,3-DNB)	99-65-0	45±4, static, 274±32 high flow; 23°C, salinity of 30 g/L	4
hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)	3980–04-6	No R_s can be calculated. Equilibrium (longer than 6 days) 6180 mL/g (HLB/water), ~0.1 cm/s, 25°C, salinity of 30 g/L	1

1. Belden et al. 2015; 2. Lotufo et al., in preparation; 3. Rosen et al., in preparation; 4. Belden et al., in preparation.

be avoided as the integrative period may be exceeded, along with increased risk associated with other field deployed devices including fouling, damage, and/or loss.

An advantage of using an integrative sampler such as POCIS is that episodic events (e.g., surface runoff, spills, and other unpredictable sources of contamination) can be sampled without the cost and challenges of trying to capture these events with trained staff at potentially remote locations. However, because of the sampling nature of the devices, it is generally unlikely to determine when the event occurred during the exposure period, or know the maximum concentration of a chemical related to the event. Integrative samplers provide data as TWA concentration of a chemical within the whole exposure period. In general, an integrative assessment such as that collected by a POCIS will be more accurate to toxicologically relevant exposure as compared to infrequent collection of discrete samples (Morrison et al. 2016).

5. Commercial availability

POCIS are commercially available from EST (St. Joseph, Missouri; http://est-lab.com; **Figure 1**). POCIS technology, covering manufacture and assembly, is the subject of United States Government patent (#6,478,961 B2) that is licensed to EST. The patent does not cover the extraction processing of the samples, however, extraction service is offered by EST.

Deployment canisters are commonly used to protect the passive samplers in the field (**Figure 1**). Canisters are commercially available from EST and hold three- or six-POCIS assembled to a holder that is secured inside the canister (**Figure 1**). The canisters are made of 304 SS mesh body with perforated 304 SS lid and bottom and are designed to protect the passive samplers from damage and allow adequate water movement through the canister. Openings in the canister are small enough to prevent large debris or organisms from entering the canister which may damage the passive samplers. Recent POCIS prices and corresponding deployment devices provided by EST are shown in **Table** 3. EST also rents canisters and holders for samplers, if desired.

Table 3. Recent POCIS and corresponding deployment device pricing from EST (EST-Lab.com)

Product	**Unit price**
POCIS (single sampler)	$65
POCIS Holder (up to three samplers)	$68
Small Canister w/ POCIS Holder (for 3 samplers)	$351
Large Canister w/ 2 POCIS Holders (for 6 samplers)	$531
Sample extraction service (each)	$50

6. Planning and preparation for field sampling

The recommended POCIS exposure duration for MC is 14-21 days (Belden et al. 2015; Rosen et al. 2017). The actual underwater deployment time in the field must be documented. Shorter deployment times should be contemplated if required by logistical constraints, but deployment time longer than three weeks is discouraged.

The analytical requirements of the study will dictate the number of passive samplers needed. Because the amount of chemical sampled is directly related to the surface area of the device, it is sometimes necessary or desirable to combine the extracts from the sorbents of multiple POCIS disks into a single sample to increase the mass of sequestered chemical for analysis. Knowledge of the mass of a chemical, total number of ng for example, which must be sampled to meet the detection criteria of the chemical analysis will affect the study design. The number of samplers needed as related to the desired environmental quantitation limit can be estimated using the following equation (Equation 2):

$$EQL = \frac{LQL \times V}{n \times R_S \times t}, \qquad \text{Equation 2}$$

Where, EQL is the quantitation limit in terms of the environmental water concentration (ng/L); LQL is the laboratory quantitation limit in terms of concentration in the extract (ng/L); V is the volume of the laboratory extract (mL); n is the number of POCIS combined; R_s is the sampling rate for the analyte of interest into POCIS (L/day); and t is time in days.

Based on the LQL obtained from the analytical laboratory, the number of samplers and enrichment (final laboratory extract volume obtained through solvent evaporation) can be determined that will allow the required EQL to be reached. Typical values for V are 0.5-5 mL and typical number of POCIS is 1 or 3.

Due to the assumption that relatively few munitions will be leaking at any given time at a given underwater military munitions (UWMM) site, compositing three for each sample and reduction of extract volume to 1 mL by the analytical laboratory is recommended. Additionally, LQL will vary based on the laboratory methodology that is conducted. In a recent controlled field validation study using 15 g sample of Composition B fragments (representing leaking UXO) as a point source, method quantitation limits as low as 2 ng/L were achieved when three composited POCIS were extracted at each sampling location (Rosen et al. 2017). For comparison, if an analytical laboratory is able to provide an EQL for MC of 100 ng/L based on a 1L water sample, the three POCIS deployed for 14 days for TNT would result in a EQL of 22.7 ng/L ([100 ng/mL x 1 mL]/[3 x 0.105 L/day x 14 days]).

The passive samplers should be transported to the field in clean airtight metal cans on blue or wet ice. This is most easily done directly by the manufacturer. If wet ice is used, it should be placed in plastic Ziploc bags to help prevent leaking which could result in the metal shipping cans rusting. It is important that the cans are not opened before use to prevent potential contamination from airborne chemicals. The cans containing the samplers should preferably be stored at <0 °C or at a minimum, kept cool (< 4 °C).

Figure 2 illustrates the preparation of commercially available samplers prior to field deployment. Samplers are shipped by the vendor to the site in a solvent rinsed paint can, in stacks of up to 12 samplers per can. On the day of the field deployment, the samplers are removed from the can, and attached to the available POCIS holder with SS nuts and bolts (also available from the vendor). The POCIS holder is then placed onto a center post on the field canister and the accompanying lid is screwed on tight. The sampling canister is then packed in a

large Ziploc bag and placed into an ice chest on blue ice to keep at 4 °C during transport to the field site.

Remove samplers from freezer and storage canister | Hand tighten samplers to POCIS holder with stainless steel screws | Place holder on deployment canister post | Screw lid on to field canister | Store cold during transport to field site

Figure 2. Pictorial of assembly of POCIS samplers in preparation for field deployment.

7. Quality Control in the Field

Field blanks are POCIS stored in airtight containers and are transported to the field sites in insulated containers filled with blue ice or wet ice sealed in plastic bags. During the deployment and retrieval operations (the time the field passive samplers are exposed to air), the lids to the field blank containers are opened to allow exposure to the surrounding air. Field blanks account for contamination during transport to and from study sites, exposure to airborne contaminants during the deployment and retrieval periods, and from storage, processing and analysis.

8. Compliance with Safety at DoD Munitions Response Sites

The conduct of field studies at UWMM sites is likely to require significant planning to ensure that the work is conducted safely and in compliance with multiple regulatory requirements. This is particularly important at Department of Defense (DoD) munitions response (MR) sites where strict compliance with the Naval Ordnance Safety and Security Activity (NOSSA) and/or other regulatory authorities may be required. It is likely that at such sites, an Explosives Safety Submission Determination Request will need to be requested and approved by appropriate staff. A dive safety plan will also likely be required for approval by appropriate authorities, and Explosive Ordnance Disposal (EOD) technicians and/or MR divers might be required on site depending on the sampling design.

9. Field deployment

A thorough cleaning of the deployment canisters before loading with the passive samplers is critical. Cleaning methods may involve a dilute acid wash (to remove salts and loosen surficial sediments and biological growth), hot soapy water wash, tap or deionized water wash, and finally an organic solvent rinse starting with a polar solvent (isopropanol alcohol or acetone) followed by a nonpolar solvent (hexane), per recommendations by Alvarez et al. (2010).

The types of equipment required for the deployment and retrieval of passive samplers can vary depending on the site and how the samplers are deployed. This is particularly important at DoD MR sites where strict compliance with the NOSSA and other regulatory authorities may be required. It is likely that at such sites, Navy EOD technicians, and trained divers trained for safely conducting fieldwork at MR sites will be required. General equipment needs are listed below:

- Ice chest/cooler for transporting the passive samplers to/from the field
- Blue ice or wet ice (sealed in plastic bags)
- Canister(s) in sealed metal cans
- Trip/field blank(s)
- Assorted tools (wrenches, pliers, cutters, saws)
- Appropriate water quality logging devices (e.g., temperature, salinity/conductivity)
- Current profiler (e.g., Nortek) to continuously log flow velocity and direction
- Weighted anchoring system or sand screws
- Signage, markings (depending on site vandalism potential)
- Field log book/sheets, digital camera
- Additional requirements associated with MR and scientific diver needs

It is favorable to have the samplers in areas with flow, as the volume of water sampled per day (sampling rate, R_s) generally increases with current velocity (**Table 2, 4**). This said, higher current velocities may also result in accelerated dilution from MC sources. The appropriate R_s should be selected according to concurrently measured, or at least historical, on site-average current velocities. Incorporation of micro-flow sensors (being evaluated under Strategic Environmental Research and Development Program [SERDP] project #ER-2542) into the canister would provide enhancement of the quantitative estimation of the TWA concentration.

Of additional critical importance to site selection is that the POCIS remain submerged throughout the deployment period. Exposure to air for many weakly hydrophobic and polar organics is of substantial significance, but this is merely a precaution for UWMM, as exposure to air during deployments for MC appear to be of relatively low risk.

10. Deployment Options

1. **From shoreline**: POCIS canisters can be placed in shallow locations near shorelines by wading, or by suspending from piers or docks. Because canisters are negatively buoyant, and can be further weighted, suspension to relatively large depths is feasible. With respect to MC, POCIS would ideally be deployed in the vicinity of known munitions that are potentially leaking MC for conservative assessment. It should be noted that considerable resources to identify leaking munitions are required and can substantially affect sampling costs. The deployment approach used to demonstrate the sensitivity of POCIS positioned around a known quantity of the explosive fill Composition B (59.5% RDX, 39.5% TNT, 1% wax) involved suspension of samplers off of a dock (**Figure 3**), which could be replicated in locations where such structures are available, eliminating the need for costly dive support.

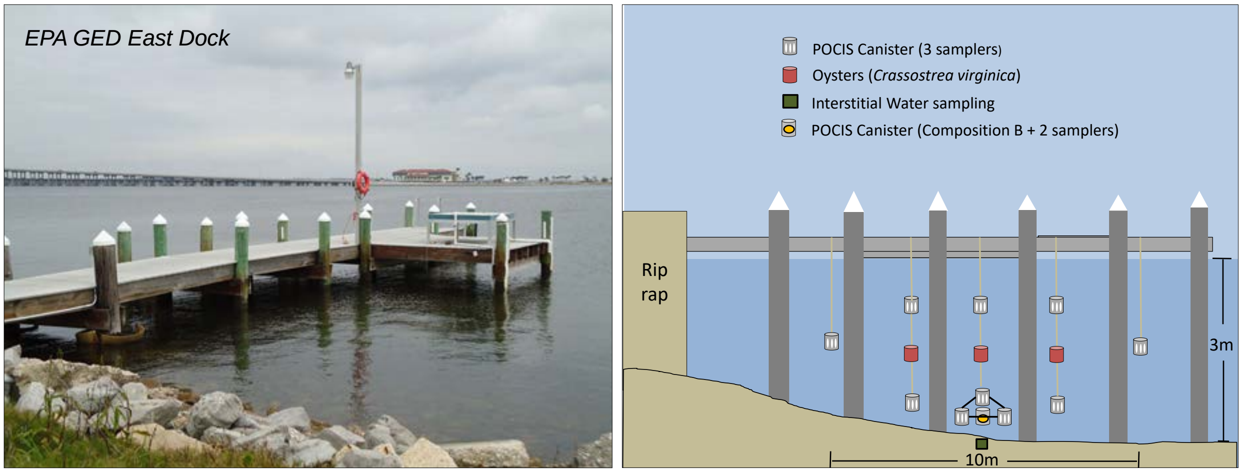
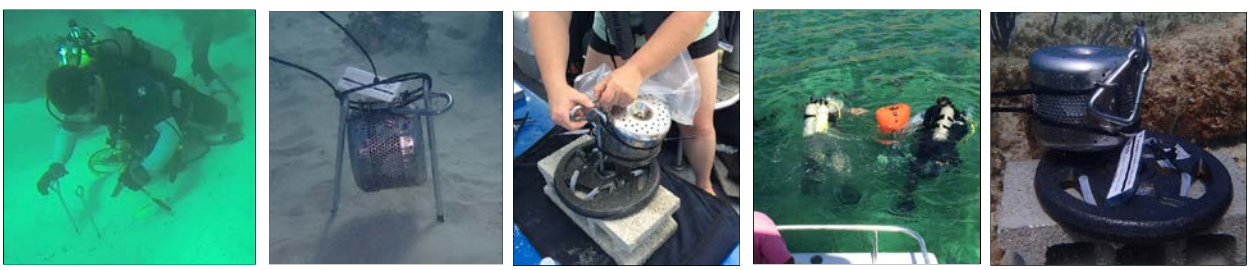


Figure 3. Photograph of EPA Gulf Ecology Division research dock where POCIS were validated using the Composition B (left); underwater representation of POCIS deployment under the EPA dock.
Note: the number and placement of samplers were for validation purposes, and not necessarily a recommendation for regulatory monitoring around a given munition/source.

2. **From boat by divers:** Boats are often necessary to reach sites in large bodies of water, and may be particularly important at DoD UWMM sites. Deployment canisters can be suspended off the bottom by attachment to piers, pilings, floating platforms, buoys, or other structures. Alternatively, canisters can be suspended from the bottom using sand screws or other anchoring systems (e.g., **Figures 4 and 5**). Divers, guided by document Global Positioning System (GPS) coordinates or by surface markers, may be required to retrieve canisters not secured to surface structures. However, the potential for vandalism at some sites may reduce feasibility of using surface markers at some sites. If GPS coordinates are not available, use of terrestrial-based reference points may be useful for marking and retrieval efforts.

3. **From boat with mooring:** A mooring, or permanent structure placed in proximity to UWMM (on biased or unbiased bases), may be used to maintain POCIS at UWMM sites during the exposure period (**Figure 4)**, with relatively limited concerns regarding vandalism and diver costs. In some cases, attachment of POCIS to moorings may be practical from a survey vessel without the need for MR diver support.

Figure 4. Deployment options for POCIS at a UWMM site including (left) screw anchors holding a POCIS sampler in place above sea floor using a grid (non-biased) deployment option; (center) placement of POCIS on a weighted brick system near potential leaking UWMM; or (right) using a mooring system in water column, potentially eliminating the requirement for cost and safety factors associated with MR divers.



(1) Munition screening with a magnetometer, followed by placement of sand screws for POCIS placement 12" above sea floor.

(2) POCIS placed above sediment following screening for munitions presence at a non-target station location.

(3) Preparation of a POCIS sampler on weighted block system for placement <12" from a potentially leaking munition.

(4) Munitions response divers using a lift bag to place a weighted-POCIS sampler near a potentially leaking munition.

(5) Close up view of a weighted POCIS sampler <12" from a potentially leaking munition.

Figure 5. Use of magnetometer followed by anchoring of POCIS canisters with sand screws (1 and 2); preparation of a POCIS weighted anchoring system, transport to the station with a lift bag, and placement adjacent to a munition (3-5).

11. Vertical Gradients

Depending on the depth of the water body, substantial gradients in the concentrations of contaminants can occur with depth. Seasonal differences in water temperature, density, and potential inputs such as effluent streams can all affect where in the water column the highest concentrations of contaminants may occur. To study this, samplers can be placed at various depths. In the case of MC, it is likely that the highest concentrations in an open water body

would be within immediate proximity (i.e. inches to a few feet) from breach munitions. The placement of samplers should be based on specific objectives of the study.

12. Biological Growth

In brackish and marine waters, a buildup of hard biofouling (e.g., barnacles) or micro- or macro-algae may occur, reducing sampling rate by POCIS. Predicting when a buildup of organisms may occur can be difficult in most brackish and marine deployments. A high degree of biofouling may make it difficult to remove the samplers, or to expect realistic sampling of available MC. If biological growth is a concern at the site, exposures should be limited to 14 days to reduce impacts on sampling rate and potentially reduced rate of uptake of target contaminants by the POCIS (**Figure 6**; Rosen et al. 2017).

Figure 6. Examples of biofouling on POCIS after (left to right), 0, 7, 14, and 28 d of field deployment at an estuarine site (Rosen et al. 2017).

13. Hardware

Many options exist for the types of hardware that can be used for securing the canisters during field deployment. Strength and protection from vandalism should be considered when selecting materials. SS hardware is preferred for prolonged water exposure and is required in marine environments to prevent corrosion. SS carabiners are recommended for securing the canisters to surface or weighted support structures, such as those shown in **Figure 4**. The hardware should be thoroughly cleaned before use with organic solvents such as acetone or hexane to remove any residual surfactants from detergent-based cleaning. Large nylon cable ties, heavy duty carabiners, or a combination of the two, can be used to secure canisters at specific locations, depending on the deployment strategy.

14. Field Observations and Measurements

Physical and chemical characteristics associated with deployment sites can be useful in the estimation of ambient concentrations and the final interpretation of the data. Water temperature, pH, conductivity, current velocity, and at least visual assessment of biofouling should be documented. Current velocity may have two-fold, or more, effect on estimation of TWA concentrations. By incorporation of current meters into the field deployment, current velocity can

be used to select the most appropriate sampling rate based on regression equations that have been derived for multiple MC (**Table 4**; Lotufo et al., in prep; Rosen et al. 2017).

General observations that can be useful for anchoring and data interpretation, as identified by Alvarez et al. (2010) include:

- Bottom conditions (soft, rocky)
- Water conditions (clear/murky, suspended sediment levels, surface film, algal growth)
- Weather/air quality during field work
- Water temperature (Harman et al. 2011)
- Condition of the samplers when retrieved

Water temperature and salinity should be measured at the beginning and end of the deployment at minimum. Monitoring of water temperature and salinity using commercially available data loggers (e.g., Onset Corp, HOBO®) attached to or in the proximity of the deployment canisters is preferable. Other water properties such as pH, total suspended solids, dissolved organic carbon, may be useful when discussing chemical speciation, distribution, and fate, but are generally not collected as part of a passive sampler study (Alvarez et al. 2010).

Table 4. Suggested sampling rates for common conventional MC based on quantified or estimated flow velocity at site.

Analyte Name (common abbreviation)	CAS number	Sampling Rate Studies, mL/day	Quantitative Certainty*
2,4,6-trinitrotoluene (TNT)	118-96-7	<9 cm/s flow = 105 9-30 cm/s flow = 18(flow rate)-50 >30 cm/s flow = 490	High
4-amino-2,6-dinitrotoluene (4-ADNT)	19406-51-0	<10 cm/s = 92.5 >10 cm/s = 324	Moderate
2-amino-4,6-dinitrotoluene (2-ADNT)	35572-78-2	<10 cm/s = 104 >10 cm/s = 474	Moderate
2,4-diamino-6-nitrotoluene (2,4-DANT)	6629-29-4	All flows= 34	Low
hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4	<7 cm/s flow = 284 7-30 cm/s flow = 8(flow rate)+270 >30 cm/s flow = 510 If longer than 21-day exposure (equilibrium) = 16400 mL/g (HLB/water)	High – less than 14 days suggested
2,4-dinitrotoluene (2,4-DNT)	121-14-2	<7 cm/s flow = 66.3 7-30 cm/s flow = 4(flow rate) + 80 >30 cm/s flow = 200	High
2,6-dinitrotoluene (2,6-DNT)	606-20-2	<20 cm/s flow = 85 20-30 cm/s flow = 4(flow rate) + 7 >30 cm/s flow = 127	High
3,5-dinitroaniline (3,5-DNAL)	618-87-1	<10 cm/s = 50 >10 cm/s = 339	Low
1,3,5-trinitrobenzene (1,3,5-TNB)	99-35-4	<10 cm/s = 77 >10 cm/s = 329	Low
1,3-dinitrobenzene (1,3-DNB)	99-65-0	<10 cm/s = 45 >10 cm/s = 274	Low
hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)	3980–04-6	Equilibrium constant valid if longer than 6 days = 6180 mL/g (HLB/water)	Low

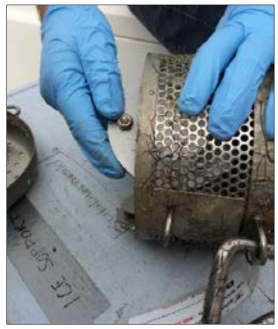
* Higher – indicates replicated studies with commercial POCIS and consideration of flow.
Moderate – indicates replicated studies with at least some work with commercial samplers and some consideration of flow.
Low – Operation only as an equilibrium sampler, no replication, no consideration of flow, or no measurements with commercial samplers.

15. Shipment, Storage, and Recovery

Following recovery of the samplers, and verification of their condition post deployment, the samplers can be shipped intact in the field canisters placed in large Ziploc bags. Alternatively, individual POCIS should be removed from the field canister and be individually packed in small Ziploc bags and then with bubble wrap to reduce likelihood for membrane puncture during

shipment (**Figure 7**). During on-site storage, recovered samplers should be kept frozen. Samplers should be shipped overnight on blue or wet ice at < 4°C to the analytical laboratory. Dry ice should not be used as it can damage the passive samplers.

Visual inspection for damage or biofouling



Removing POCIS from field canister

Individual sampler preservation/bagging to prevent contamination

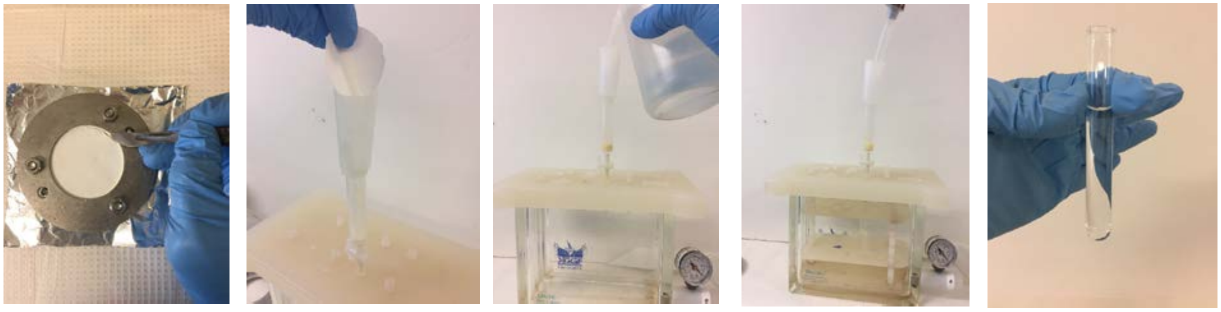
Bubble wrap and shipment at 4°C to prevent damage

Figure 7. Upon recovery, samplers are inspected for damage and biofouling, carefully removed from the field canister, photo-documented, and individually wrapped in labeled Ziploc bags. Prior to shipment, each bag is wrapped in bubble wrap to minimize risk of membrane damage during transport.

16. Processing of the POCIS

The first step in chemical analysis is to perform an extraction procedure for the POCIS. The extraction methods for the recovery of chemicals from the POCIS typically conducted with MC involves opening the POCIS, rinsing the sorbent into an empty SPE tube, and then eluting with solvent that is captured and evaporated to a small known volume (**Figure 8**). It is recommended that large empty cartridges with capacities of 15 mL or greater be used, or alternatively 6-mL SPE tubes, and a tight-sealing reservoir is placed on top to allow for adequate volumes of rinse and elution solvent (**Figure 9**). Prior to rinsing the sample into the column, a frit is placed in the bottom of the SPE cartridge (Oasis HLB sorbent).

The cartridge and frit are rinsed with the solvents to be used during the POCIS extraction and dried. The flow of solvent and water through the cartridge can be achieved using a vacuum manifold (**Figure 9**). The POCIS is opened over a funnel and ultrapure water is used to transfer the sorbent into the cartridge. The water does not need to be retained. The sorbent is dried by vacuum to remove all traces of water before extraction. Elution of analytes can be conducted by several solvents (DeTata et al. 2013). Although POCIS extraction has been recommended to use 40 mL of methanol, smaller volumes of ethyl acetate and acetonitrile (10 mL recommended) have been shown to readily extract MC from the small mass of sorbent recovered from a single POCIS (DeTata et al. 2013, Belden et al. 2015).



POCIS are dismantled either by removing bolts or by using a sharp knife to cut the membrane. The stainless steel knife and aluminum foil used to catch any leaked material should be solvent washed.

The sorbent contained in the POCIS is carefully transferred into an empty solid-phase extraction (SPE) tube that contains a frit. The tube and frit must be cleaned/new and solvent washed prior to use. Water and vacuum can be used to collect all sorbent against the frit. The water is discarded and the vacuum is pull for a few minutes to dry the sorbent.

A test tube is then placed under the SPE tube. Analytes on the sorbent are eluted using solvent and collected in the test tube. The volume of the solvent can then be reduced under a stream of nitrogen to allow for an accurate final volume and enrichment of the sample.

Figure 8. Steps required to remove sorbent from POCIS sampler, collect sorbent on SPE tubes, and elute the analytes into a test tube for analysis.

For GC analysis, ethyl acetate is recommended as drying of the solvent with anhydrous sodium sulfate and evaporation is quicker. For LC analysis, laboratories may choose acetonitrile to limit the need for solvent exchange. For MC analyses, evaporation to dryness should be avoided. Note: this process is analogous to the final steps of analysis using SPE extraction. If a laboratory has an SPE extraction analysis, their current procedures can be used once the sorbent is rinsed into the SPE column. Once the extract is obtained, analysis can be performed using any methodology accepted for MC analysis (e.g., EPA 8330, EPA 8095).

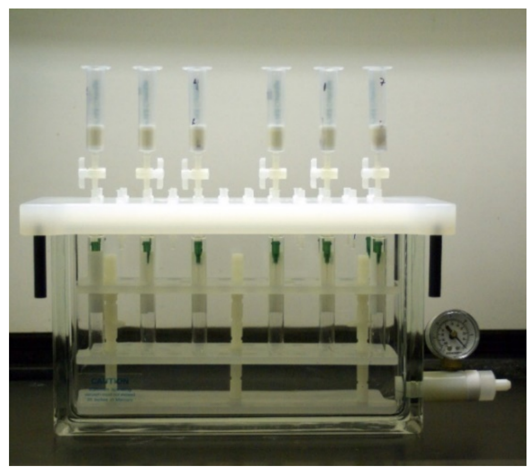


Figure 9. POCIS extraction vacuum manifold for SPE. SPE cartridges, shown on top of manifold, are available from Waters Corp.

17. Sample Composites

Because of the small surface area of the POCIS, which is related to the amount of chemical sampled, it is a common practice to composite the extracts of two or more POCIS into a single extract in order to increase the amount of chemical present in the extract for detection. This practice aids in the detection of compounds expected at very low concentrations in the environment and when the sampling rate for a target chemical is very low or short exposure times were used resulting in minimal volumes of water extracted. Typically, individual POCIS are extracted as described above and the extracts are combined at the evaporation step. The three POCIS that are housed in the commercially available small POCIS canister have been generally successful for monitoring of MC at UWMM sites thus far (Rosen et al. 2016, 2017).

18. Estimating Water Concentrations from POCIS Data

The analytical laboratory will provide the user chemical concentration data in a raw form that will require additional data processing in order to quantify water concentrations. The data will usually be reported as ng of a chemical per sampler, where the sample will be the passive sampler extract. If the data are reported as an extract concentration, ng/sampler can be calculated by multiplying by the volume of the extract.

Estimating water concentrations from POCIS data is contingent on the availability of experimentally-derived R_s data. Based on the R_s values presented in **Tables 2 and 4** for multiple MC, concentrations can be expressed on a ng/L TWA basis.

Assuming that the chemicals of interest sampled by the POCIS remain in the integrative phase of sampling for the deployment time, the use of the integrative uptake model for the calculation of ambient water concentration is justified (see Equation 1 above).

In cases where R_s data for a specific chemical are not available, the result should be reported as mass of chemical sampled per POCIS (ng/POCIS), resulting in a more qualitative estimate of the TWA, but can be used to indicate the presence or absence of a chemical. With regard to the detection limit, this information can be useful in determining the relative amounts of a chemical present at each site (ranking of sites).

19. Data Analysis and QA/QC

Coordination with analytical lab and holding times

The study needs should be discussed with the analytical laboratory before beginning fieldwork. Many analytical laboratories have not worked with POCIS and may be uncertain of how to process the media or extract chemicals from it. POCIS extracts are generally easier to work with than samples of other environmental matrices and should be analyzed by standard instrumental techniques the lab uses for other matrices, such as water or sediment extracts. The sorbent used in the POCIS is also commonly used in SPE applications, and therefore, should be readily processed in the same way that most labs process SPE used for extraction of contaminants from water samples. The commercial vendor of the POCIS offers sample extraction as a service. See **Section 16** for a description of extraction procedures.

The reporting procedures of a laboratory should be discussed as many laboratories use automated reporting systems set up to report in the units of ng/L of water. These units are not suitable for a passive sampler extract as the desired units should be reported as total ng of chemical per POCIS or combined replicate POCIS, as in some cases, POCIS deployed at the same site may be pooled into a single extract to increase sensitivity or decrease variability. The unit of ng/POCIS is required for the calculations to estimate ambient water concentrations. These instructions will need to be communicated to the laboratory.

Once frozen, POCIS have a longer holding time than water samples. They should be held up to 72 hours at 4°C while transferred to the environmental laboratory. Once at an analytical laboratory, they can be frozen for up to 28 days prior to extraction and analysis.

Quality Control

Quality control for POCIS will have the same general procedures as for other types of samples. For each sampling trip, a blank passive sampler (field blank) should be subjected to all phases of the field and transport experience. During the deployment and retrieval operations (the time the field passive samplers are exposed to air), the lids to the field blank containers are opened allowing exposure to the surrounding air. Field blanks account for contamination during transport to and from study sites, exposure to airborne contaminants during the deployment and retrieval periods, and from storage, processing and analysis. These samples should be extracted and analyzed along with field samples in an effort to check for contamination.

Extraction and procedural efficiency should be measured using surrogates in each sample. Preferentially, stable isotopes of MC should be used, or other related compounds suggested by the analytical method (EPA 8330 or 8095). As with all standard methods, procedural blanks, spikes and spike duplicates should be conducted at a frequency of at least 5% of samples extracted. Spiking analytes into the sorbent to conduct laboratory spikes can be challenging due to dispersal. Spiking using a solvent carrier can be conducted directly to sorbent followed by careful mixing. Alternatively, a water carrier can be used to load the MC on the sorbent after the sorbent is loaded into an SPE cartridge (similar to a standard SPE extraction).

Quality control for instrumentations will be based on the chosen analytical technique and will not be different than required for other matrices.

Data management and analysis

Data management and analysis will be conducted similarly as per all other matrices. The exception as noted is that concentrations should be reported as mass of analyte/POCIS. From these units, water concentrations can be calculated using the standard equations for converting mass accumulated to a TWA concentration, provided in **Sections 3**, with the inclusion of flow rate-specific sampling rates, if available, as shown in **Section 14**.

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